The Catalytic Activity of Copper—Part III.

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The catalytic action of the metallic oxides upon alcohols has been very completely studied by Sabatier and Mailhe* in the qualitative way. They showed that the alcohols in contact with oxides at 200°—400° C. can undergo two sorts of decomposition—(*a*) dehydration, (*b*) dehydrogenation—and they were able to classify oxides in respect of these two reactions. The following Table is extracted from their paper, and includes only oxides the activity of which is preferentially dehydrogenating:—

	Activity (ethyl alcohol, at 340–350° C.).	Composition of gaseous product.	
		Ethylene.	Hydrogen.
		volume per cent.	volume per cent.
Ferric oxide	32	14	86
Zinc oxide	6	5	95
Manganous oxide	3·5	0	100
Magnesium oxide	Traces only	0	100
Copper reduced from cupric oxide.	110	0	100

The activity is expressed in arbitrary units.

Only the oxides at the extreme ends of the list given by Sabatier bring about one reaction exclusively. For example, thoria is exclusively dehydrating, and magnesia is the only exclusively dehydrogenating oxide. However, the dehydrating activity of the above oxides is small.

The present communication describes the effect upon the catalytic (dehydrogenating) activity of copper, of admixing these oxides in varying proportions. The effect of volatile additions, such as hydrogen and water vapour, has been previously described.†

Apparatus, and Preparation of the Catalyst.

It was convenient in the present work to use a smaller catalytic surface than previously, and hence a gas-meter working with smaller quantities of gas was necessary. The diagram (fig. 1) shows the form of meter found to give satisfactory results.

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* 'Ann. de Chim. et Phys.,' vol. 21, p. 289 (1910).

† 'Roy. Soc. Proc.,' A, vol. 98, p. 13; vol. 99, p. 412.

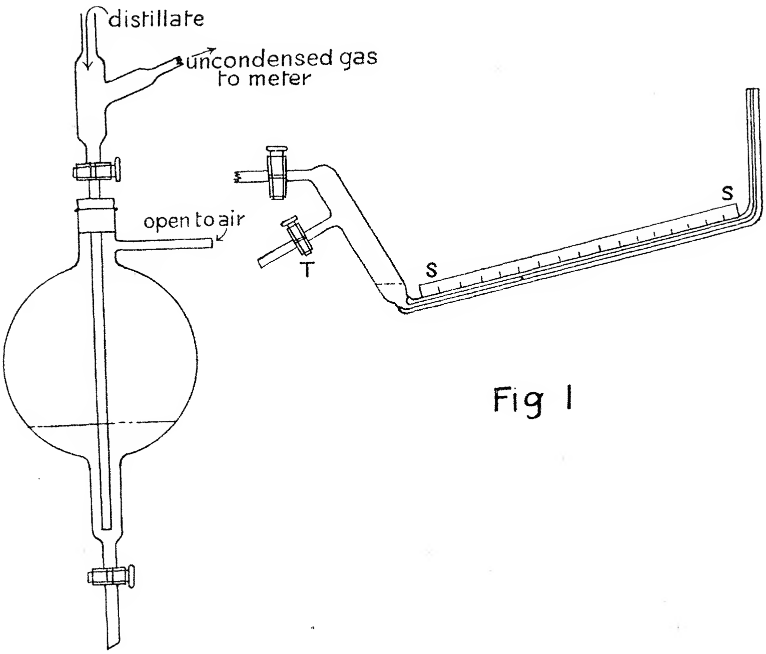

Fig 1

In order to give a motion of about 2 cm. on the scale SS, an evolution of about 0·2 c.c. of gas was required. The increase of pressure in the apparatus consequent upon this motion was too slight to cause an appreciable change in the rate of boiling of the alcohol below the reaction tube. The mode of working consisted in depressing the chronograph key, and simultaneously opening the tap, T, for a moment, when 2 cm. of the scale had been covered by the liquid. The liquid then fell back to its zero position, and a new reading was taken, and so on. If the capillary tube is kept clean the motion of the liquid is quite regular. This meter replaced the "bubbler" formerly used. The one-litre flask for temperature control was retained between the meter and the rest of the apparatus. The use of this sensitive gauge makes it impossible to allow the condensed alcohol to remain in the system of the apparatus, as the increasing volume of the distillate would be registered as a gas evolution. A special receiver (see fig. 1) was devised to meet this difficulty.

A fresh sample of ethyl alcohol taken from a large stock of 3 litres was used for each activity test. The amount necessary for one test (70 c.c.) was boiled vigorously for 2 hours to expel dissolved air, in an apparatus directly connected with the boiler supplying alcohol vapour to the reaction tube. The hot alcohol was run in through a tap immediately before a test was begun. A constant current was used throughout for the heating coil in the boiler.

The reduction of the catalyst was carried out with carbon monoxide, it having been previously shown (*loc. cit.*) that other reducing agents complicate the catalytic effect of the reduced copper. A carbon monoxide generator, in which the gas was made by mixing concentrated sulphuric and formic acids at 60° C., was directly connected with the reaction tube. The gas passed over soda-lime and calcium chloride before being admitted to the main apparatus.

After many experiments all methods of preparing the contact material by impregnation of porous rods from solution were abandoned. In the former work with pure copper the catalyst surface was made by impregnating gas-mantle supports in an aqueous solution of copper formate, drying, and then igniting to oxide at 250° C. This method is not satisfactory for the study of mixed catalysts, since it is practically impossible to choose conditions that prevent a separation (owing to differential surface action) of the constituents of the mixture on drying.

For example, a porous rod was soaked in an ammoniacal solution of copper formate and silver oxalate, in which the ratio Cu/Ag was 100/5. After drying and ignition at 250° C., the black deposit was dissolved in hot dilute nitric acid. Only traces of cloudiness were produced in the solution by the addition of ammonium chloride. On breaking the cleaned rod a black ring of silver was discovered below the surface of the rod, showing clearly that the silver oxalate had retreated from the copper during the drying. The following method gives complete control over the composition of the catalytic deposit, and at the same time allows the catalyst to be out of contact with the material of the rod.

About 20 c.c. of a solution of copper sulphate (containing about 10 grm. of the hydrated salt in 100 c.c. of solution) were mixed with a quantity of a solution of the sulphate, or other soluble salt of the metal whose oxide is to be mixed with the copper. The mixed solution was then run from a burette slowly into 100 c.c. of vigorously boiling 10 per cent. sodium carbonate solution. Cupric oxide, mixed with the oxide or carbonate of the added metal, was at once precipitated. In the excess of hot sodium carbonate solution used there remains throughout the precipitation substantially a constant concentration of hydroxide formed by hydrolysis. Sodium carbonate was therefore an advantage over hydroxide solution in providing more uniform conditions of precipitation.

The precipitate was collected on a filter and washed until a small portion held on a clean platinum wire gave no yellow colour to the Bunsen flame. The washing was in most cases laborious, and was best accomplished by boiling in portions of fresh water and not by washing on the filter-paper. Oxides such as magnesia and zinc oxide, wash out, and it is consequently not easy to predict with exactness the composition of the final oxide mixture from the proportions of solutions taken. Mixtures free from sodium, and containing by weight more than 10 per cent. of magnesia, or 8 per cent. of zinc oxide, could not be prepared owing to this leaching during the washing. The oxide mixtures were finally dried in the steam-oven and analysed by the usual methods.

A mantle-rod, as previously used for supporting the catalyst (*loc. cit.*), was cleaned by ignition, cooled and moistened with pure oleic acid. A sample of mixed oxide was then applied to the rod by rubbing with a soft rag, the fork of the rod serving as a convenient handle. The rod was then ignited to low redness by passing through a Bunsen flame in such a position that, within the flame, the cupric oxide is reduced to metal, and on emerging from the flame is re-oxidised to black oxide. By this means silver and bismuth were given an opportunity to become alloyed with the copper, while non-reducible oxides, such as magnesia and zinc oxide, form saturated solutions in the metal; iron and manganous oxides become re-oxidised with the copper on passing out of the flame.

After cooling, the oleic acid treatment was repeated, until the rod was quite black with the closely-adhering copper oxide. The rod was fully charged, as a rule, after three treatments. Full charge was easily demonstrated by testing the activity, and then re-treating. In no case was the activity increased by more than 2 per cent. by re-treatment after three initial treatments.

To test the reproducibility of the material two rods were prepared, each charged fully with pure copper oxide. Both rods gave the same activity to within 3 per cent. The oleic acid gave no ash on ignition in air.

The deposit consisted of a comparatively thick film, and there is no doubt that the outer layer was not in contact with the material of the rod; the mixture was therefore virtually "unsupported." The rod so prepared was used for each test in place of the eight rods formerly used. It is easy to arrange a single rod centrally in the reaction tube and so secure a minimum amount of eddying in the flow of the vapour. The average amount of copper on each rod was 0·002 grm.

Before an experiment the whole apparatus, up to the gas-meter, was tested tight to a reduced pressure of 60 cm. of mercury, and then filled with nitrogen as in previous work. The temperature in the reaction tube was then raised and kept steady at 205 ± 1°C., while carbon monoxide was passed through the reaction tube for some minutes. The temperature was then raised again and kept constant during the activity test, the hot alcohol being run into the boiler immediately before the reaction temperature of 260° C. was reached.

The chronograph record started in all cases from the time when the first drop of distillate appeared in the condenser, and continued for a period of 45 to 60 minutes. The activity, in most cases, was quite constant for 25 to 30 minutes, after which it slowly decayed, owing, undoubtedly, to sintering of the catalytic surface. This somewhat rapid onset of decay is the only disadvantage in using catalytic material prepared in the manner described.

The detailed results are now given under separate headings for each mixture. The activities, in all cases, are for reduction by carbon monoxide at 205° C., and reaction with ethyl alcohol at 260° C. They are expressed in arbitrary units by dividing 100 by the distances between marks on the chronograph record. In the following Tables the activities at constant intervals during the period of observation are recorded.

The proportions of oxide are calculated in molecules of oxide to 100 atoms of copper. For this purpose the copper is taken as monatomic, and the oxide given its simplest formula.

1. *Copper—Sodium Carbonate Mixtures.*

It was thought advisable to investigate the effect of leaving small quantities of the precipitant in the prepared oxide.

Three preparations were made under the same conditions as for oxide mixtures:—

(1) Oxide washed once with cold water; contained 2·8 per cent. sodium carbonate.

(2) Oxide washed five times on the filter-paper with hot water; contained 0·8 per cent. sodium carbonate.

(3) The oxide was washed quite free from sodium salts (this preparation gave the comparison activity of pure copper).

The sodium salts were estimated by depositing the bulk of the copper electrolytically, the last traces being then removed by hydrogen sulphide, and the liquid evaporated to dryness. The residue was weighed as Na_2SO_4 after treatment with ammonium carbonate in the usual way.

To 100 Cu, 0·5 Na_2CO_3.	1·6 Na_2CO_3.	Pure copper.
No activity (nor with isopropyl alcohol)	12·0 12·5 12·5 12·5 12·7	44·5 45·5 47·0 44·5 44·7

The drastic effect of small quantities of sodium salts on the copper recalls a similar action on precipitated alumina when this is used as a dehydrating agent for the preparation of ethylene from alcohol.* No doubt the effect originates in the same cause in both cases.

2. *Copper—Magnesium Oxide.*

To 100 Cu, 1·58 MgO.	2·4 MgO.	7·8 MgO.	12·4 MgO.	15·5 MgO.
6·0	39·5	58	75·0	120·0
4·7	38·0	58	77·0	119·5
4·6	41·0	55	76·0	117·0
3·5	40·8	56	79·0	121·0
	40·0		74·0	114·0
	40·7			

3. *Copper—Ferric Oxide.*

To 100 Cu, 1·02 Fe_2O_3.	3·75 Fe_2O_3.	6·6 Fe_2O_3.	20·4 Fe_2O_3.
12·8	9·9	17·0	13·0
12·0	10·0	17·0	14·0
12·4	10·1	16·0	13·2
13·0			13·0
12·5			

4. *Copper—Zinc Oxide.*

To 100 Cu, traces of ZnO.	0·77 ZnO.	2·06 ZnO.	4·65 ZnO.
About 1·0	No activity	24·5	27·0
		28·0	26·5
		26·0	28·0
		27·5	27·0
		27·0	27·5

5. *Copper—Manganous Oxide.*

To 100 Cu, 0·42 MnO.	0·89 MnO.	1·6 MnO.	8·2 MnO.	18·8 MnO.	33·0 MnO.
29·0	84·0	51·0	57	52·5	64·1
27·0	72·0	52·0	55	53·0	63·8
30·0	62·0	51·5	50	53·0	65·0
28·0	58·0	51·0	54		64·5
29·0	55·0				
	47·5				
	43·0				

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* Senderens, 'Ann. de Chim. et Phys.,' vol. 25, p. 476 (1912).

The following Tables show the mean activity calculated from the preceding Tables, and the activity corrected for the dilution of the copper. For this purpose the following specific gravities were used—

Cupric oxide	6·35
Magnesia	3·19
Zinc oxide	5·6
Ferric oxide	5·17
Manganous oxide	5·10

Composition of catalyst.		Mean activity.	Duration of constant activity in minutes.	Corrected activity.
	(To 100 Cu)			
MgO	1·58	4–5	(Recorded for 25 minutes)	4–5
	2·4	40·0	29	41·0
	7·8	55·0	26	59·0
	12·4	77·0	30	86·0
	15·5	121·0	26	140·0
ZnO	traces	1·0	—	1·0
	0·77	inactive	—	—
	2·06	25·0	25	25·5
	4·65	28·0	30	29·5
Fe_2O_3	1·02	12·6	27	12·6
	3·75	10·5	17	11·6
	6·6	17·8	15	21·0
	20·4	13·0	23	20·0
MnO	0·42	30·0	30	30·0
	0·89	84·0–47·5	unstable	—
	1·60	51·5	19	52·5
	8·2	54·0	26	60·0
	16·6	56·5	35	68·0
	33·0	64·0	53	92·5
Na_2CO_3	0·5	inactive	—	—
	1·6	12·5	26	12·5
Pure copper		—	—	45·5

These results are shown graphically in figs. 2 and 3: fig. 3 shows the relation of activity to percentage of oxide on a larger scale for small additions of oxide.

The mixtures containing manganese oxide were precipitated from mixed solutions of cupric and manganous sulphates. After ignition to low redness on the rod the manganese is present as manganic oxide, Mn_2O_3.*

The effect of carbon monoxide on this oxide of manganese and on ferric oxide, when each is mixed with cupric oxide, was ascertained in separate experiments.

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* R. J. Meyer and K. Retgers, 'Zeit. anorg. Chem.,' vol. 57, p. 104.

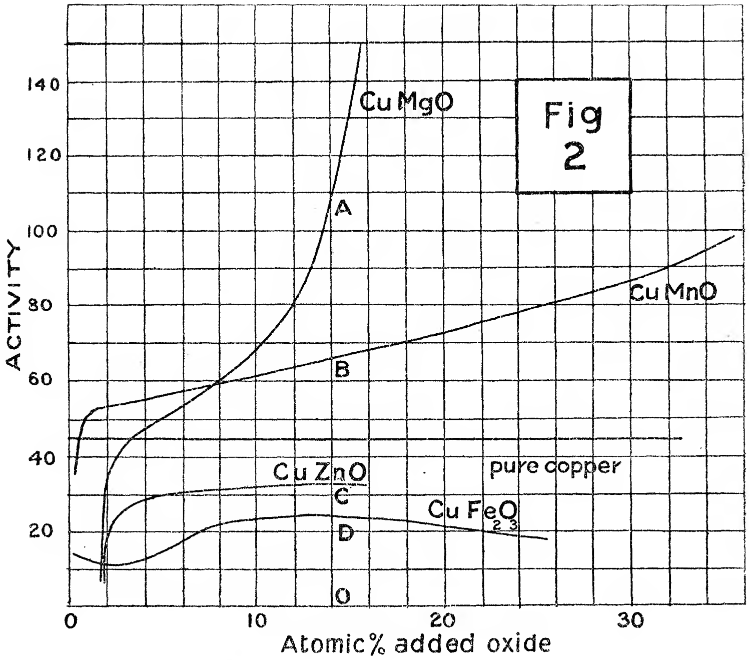

Fig 2

ACTIVITY
140
120
100
80
60
40
20
Cu MgO
A
B
Cu MnO
C u ZnO
C
pure copper
Cu FeO 2 3
D
O
0
10
20
30
Atomic % added oxide

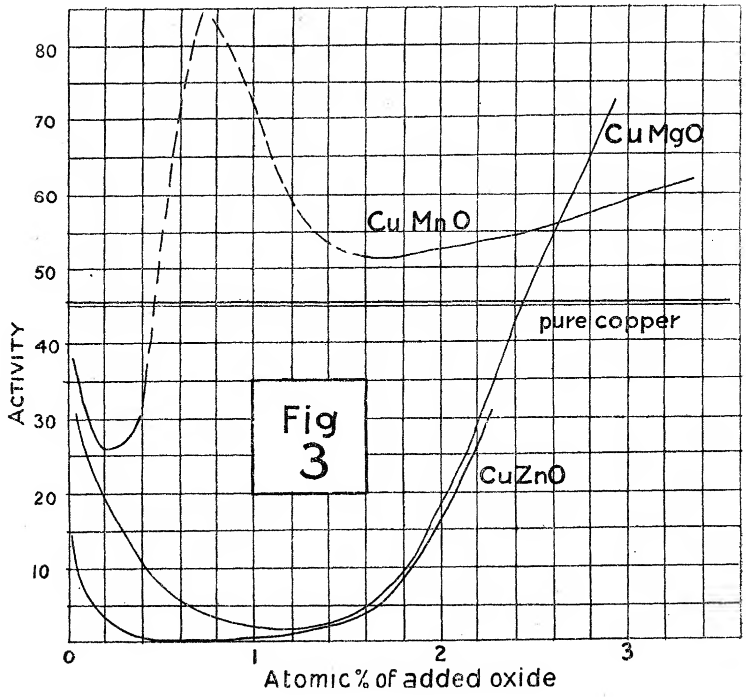

Fig 3

ACTIVITY
80
70
60
50
40
30
20
10
Cu MgO
Cu Mn O
pure copper
CuZnO
0
1
2
3
Atomic % of added oxide

A mixture prepared in the same way as for activity tests was ignited to redness in air, and carbon monoxide was then passed over the mixture contained in a weighed glass tube kept at 205° C. After 1 hour practically no carbon dioxide was leaving the tube, which was then cooled while the gas continued to pass and finally sealed off and re-weighed.

The following results were obtained:—

0·484 of mixed cupric and ferric oxides, containing 29·5 per cent. Fe_2O_3 and 70 per cent. CuO (estimated separately) lost 0·0745 grm. on reduction. Per cent. loss = 15·4. Calculated loss for reduction of cupric oxide alone = 14·5.

There appears, therefore, to be only a slight reduction of ferric oxide at the temperature used for reductions.

0·239 grm. of mixed manganic and cupric oxides containing 66·2 per cent. CuO and 33·1 per cent. Mn_2O_3 (estimated separately) lost 0·0395 grm. on reduction. Per cent. loss = 16·5. Calculated for reduction of copper oxide alone 13·6 per cent.; and for manganic oxide to manganous oxide 3·3 per cent.; total loss 16·9 per cent.

Therefore the conditions used for reduction of the copper oxide produce manganous oxide.

If heated in a rapid stream of inert gas, magnesium carbonate is completely decomposed at 200° C.,* so that it is extremely improbable that the magnesia in the mixtures retains the carbon dioxide formed by the reduction of the copper oxide. *A fortiori* the other less basic oxides used are not likely to be converted into carbonates.

As will be emphasised in the following discussion, considerable importance attaches to the solubility of the material added to the copper in this metal. Hence the activity of preparations containing a metal known to be soluble in the copper was tested. The metals silver and bismuth were chosen, as these have oxides readily reducible by carbon monoxide at 205° C. The alloys examined had the following compositions (in atomic percentage):—

	Copper-silver Ag		Copper-bismuth Bi
(1)	0·30	....	0·345
(2)	0·375	....	0·57
(3)	0·52	....	0·88
(4)	1·58	....	4·00

With the exception of the mixture of Bi-content, 0·345 per cent., which showed very feeble activity, all of these alloys were completely inactive. Kursanow† has shown that silver may give solid solutions in copper up to

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* Abegg and Auerbach, 'Handbuch d. anorg. Chem.,' vol. 2 (ii), p. 67.

† 'Zeit. anorg. Chem.,' vol. 68, vol. 123 (1910).

4 per cent. of silver, while K. Jeriomin* has indicated that bismuth can be present as solid solution up to 0·5 per cent.

The above experiments indicate the drastic nature of the effect of solutes on the activity of the copper. Sabatier and Mailhe (*loc. cit.*) found bismuth to be quite inactive upon primary alcohols.

Discussion of Results—the Properties of "Promotors."

The list of oxides previously given shows that the activity of the pure oxides is usually much less than that of copper. Ferric oxide has the greatest activity, which is only about one-third of that of copper. The oxides, therefore, must be deficient either in adsorbing power or in density of radiation of about 1·0 μ wave-length (see previous papers, *loc. cit.*).

It is known, however, that oxides such as magnesia, alumina, and ferric oxide adsorb water, and therefore probably alcohol, to a markedly greater extent than metals. We may therefore assume that infra-red radiation of appropriate wave-length is emitted by the oxides only to a slight degree compared with copper. In short, the order of the oxides in the list is one of decreasing emissivity for wave-lengths about 1 μ, and therefore one also of decreasing adsorbing power for this wave-length.

Hence, if a nucleus of copper be surrounded by a *thin* layer of one of these oxides, the adsorbing power of the complex will probably be greater than that of the copper alone, but this favourable increase may be more than counterbalanced by the opacity of the oxide film to the radiation from the copper core. As the proportion of oxide added is increased, the number of copper nuclei will tend to increase; in other words, the oxide peptises the copper. This peptising action will have the effect of keeping the film of oxide thin over a wide range of concentration of the oxide.

The requirements of a "promotor" are thus seen to be: (1) transparency to the radiation from the main catalyst; (2) higher adsorbing power than the main catalyst. A higher peptizing power is an advantage, though it is not essential. Of the oxides examined in the present work, only magnesia and manganous oxides satisfy these requirements.

If, as is quite probable, the same atomic concentration of copper in any oxide implies approximately the same degree of dispersion (in the colloidal sense), then the right-hand portions of the curves (fig. 2) will be in the order of the transparency of the oxides to the copper radiation. These transparencies are measured, in fact, approximately by the ordinates AO, BO, CO, etc.

It will be noticed that the order of activity as given by Sabatier, which is assumed to be also an order of decreasing adsorption of the proper radiation, is followed in the inverse way by these ordinates. Data on the transparency of metallic oxides to infra-red radiation are scanty, but Königsberger[*] found the following transmission ratios $= \frac{\text{(energy incident)}}{\text{(energy transmitted)}}$ for 0·5—4·0 μ.

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* 'Zeit. anorg. Chem.,' vol. 55, p. 413 (1907).

Ferric oxide	0·101
Manganite (presumably MnO (OH))	0·160

These results are of the same order as the ratios of the ordinates for ferric and manganous oxides in the curves given above.

The Activity with very low Concentration of Oxide.

When cupric oxide containing about 1 per cent. or less of another oxide is reduced to metal it is possible that the oxide remains dissolved in the metallic copper, and does not separate to form a second phase.

The form of the solution may be "true" or colloidal,[†] but in either case the surface energy of the copper will be diminished by the solute, just as in the case of silver and bismuth admixtures, and adsorption correspondingly reduced.

It is not easy to demonstrate a diminished adsorption for alcohol, but the reduced adsorption for atmospheric oxygen in the case of these preparations was strikingly shown in the following way. In all cases the catalytic preparations were allowed to remain in the reaction tube until this was cold, the exit taps being open and air admitted. While, in these circumstances, an active preparation was always much tarnished, and even blackened deeply by oxidation, an inactive preparation remained quite bright and untarnished, and in general could only be oxidised at room temperature by several days' exposure. The preparations of lowest oxide-content in magnesia, zinc oxide, and manganous oxide, as well as all the silver and bismuth preparations, all showed similar behaviour. Photographs of these preparations are given in fig. 4.

According to the above discussion the curves (figs. 2 and 3) can be interpreted as follows:—

(a) *Ferric Oxide-Copper.*—Oxide quite insoluble in metal, but very opaque to its radiation. Activity of mixtures increased beyond 3·5 per cent. of ferric oxide owing to peptization of the metal.[‡]

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[*] 'Phys. Zeit.,' vol. 4, p. 495 (1904).

[†] For a discussion on the solubility of oxides in copper, see 'Journ. of the Inst. of Metals,' vol. 8 (2), pp. 222, 248 (1912).

[‡] Sabatier and Mailhe found that ferric-oxide reduced the dehydrating activity of alumina very markedly ('Ann. de Chim. et Phys.,' vol. 20, p. 300 (1910)).

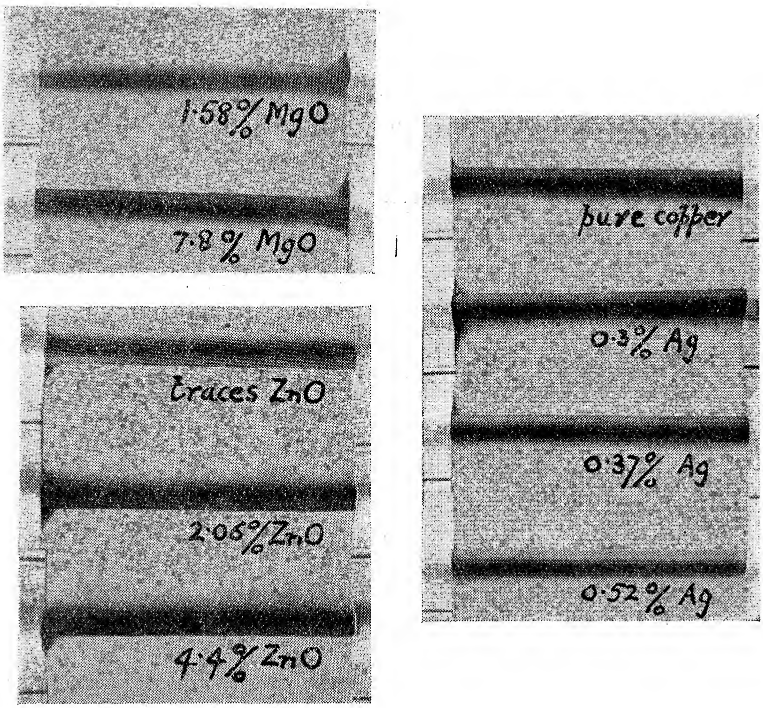

FIG. 4.

(b) *Zinc Oxide-Copper.*—Oxide soluble up to 0·5 per cent. Amounts of zinc oxide from traces up to 0·5 per cent. destroy the activity, which is gradually regained with increasing oxide-content, owing to the formation of two phases. The activity is throughout, however, lower than that of pure copper.

(c) *Manganous Oxide-Copper.*—Oxide only very slightly soluble. The peak at 0·8 per cent. remains unexplained. The value of the activity of this concentration was very unstable, falling from 84 to 47·5 in 17 minutes. Manganous oxide is a weak "promotor" at all concentrations greater than 1 per cent.

(d) *Magnesium Oxide-Copper.*—Oxide soluble up to 1·1 per cent. The oxide is a strong promotor at all concentrations greater than 2·5 per cent.

It is to be noticed that the activities of mixtures, the concentrations of which lie on the steep parts of the curves, are all more or less short lived.

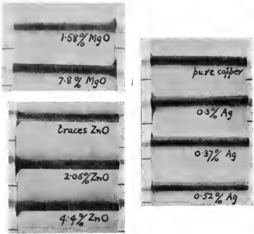
1·58% MgO
7·8% MgO
traces ZnO
2·06% ZnO
4·4% ZnO
pure copper
0·3% Ag
0·37% Ag
0·52% Ag

FIG. 4.